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Infrared absorption spectra of samarium mono-, di-, and tri-glycolates

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Infrared absorption spectra of mono-, di-, and tri-glycolates of tripositive samarium have been studied in the region 4000-250 cm^{-1} in KBr pellets with a Perkin-Elmer 521 spectrophotometer, for the first time. About twelve bands in each glycolate have been observed and assigned to different modes of vibrations. Comparison of data reveals that vibrational frequencies are independent of the co-ordination number of the metal in the region 4000-700 cm^{-1}. The number of metal-oxygen vibrational modes in the region 700-250 cm^{-1} suggests C_{2v}, V_h, and D_3 symmetries for samarium mono-, di-, and tri-glycolates, respectively.

1. INTRODUCTION

Recently, the analysis of the vibrational spectra of glycol derivatives of uranium (Rosado *et al* 1969), lead (Nakayama *et al* 1968), and other metals (Larson 1965, Miyake 1959) has appeared in the literature. A survey of the literature reveals that no work on infrared absorption spectra of glycol derivatives of samarium has been carried out so far. The infrared study of rare earth in different environments would give an idea about the structure, amount of metal-oxygen bonding and the vibronic contribution to the electronic spectra. The present communication reports the infrared absorption spectra of

Samarium mono-glycolate (SMG)	$Sm(OPr^i)_3$ + propane 1, 3 diol (OPr^i) $Sm(C_3H_6O_2)$ in molar ratio 1:1.
Samarium di-glycolate : (SDG)	$Sm(OPr^i)_3$ + 2, 3 dimethyl butane 2, 3 diol ($C_6H_{13}O_2$) $Sm(C_6H_{12}O_2)$ in molar ratio 1:2 and
Samarium tri-glycolate : (STG)	$Sm(OPr^i)_3$ + propane 1, 3 diol ($C_6H_{15}O_4$) $Sm(C_3H_6O_2)$

in molar ratio 1:3, for the first time. The results have been discussed in the light of theoretically calculated different modes of vibrations. An attempt has been made to investigate the metal-oxygen bonding in these complexes.

2. Experimental

$Sm(OPr^i)_3$ was prepared from samarium chloride by sodium alkoxide method (Sankhla *et al* 1965). The reactions of $Sm(OPr^i)_3$ with propane 1, 3 diol and 2, 3 dimethyl butane 2, 3 diol in different molar ratios have been described elsewhere (Sankhla & Kapoor, 1965).

Spectra from 4000-250 cm^{-1} of the powdered samples, less than 5μ in particle size, in KBr pellets were recorded by using a Perkin-Elmer model 521 spectrophotometer purged with dry air. 400 mg of KBr and an equivalent molar concentration of 1.8 mg of glycolates were pressed in an evacuated die under a total force of 10 tons for 2 minutes. No annealing was done as at 100-110°C a reaction with KBr may occur. The spectra were recorded at 25°C. The 25°C temperature was not controlled but it remained nearly constant in the infrared beam of the spectrophotometer in ambient surroundings.

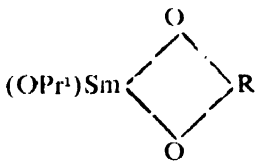
3. Results and Discussion

The observed vibrational frequencies have been tabulated in table 1. The intensities of the bands have been classified as weak(w), medium(m), strong(s), weak broad(wb), strong broad(sb) and have been indicated in the table 1.

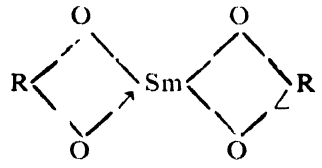
Table 1. Observed infrared frequencies, relative intensities and proposed assignments of samarium glycolates

SMG	SDG	STG	Assignments
—	~3400(sb)	~3400(sb)	bonded OH stretch
2953(w)	2960(w)	—	asym. CH_3 stretch
—	—	2930(w)	CH_2 stretch
—	2872(w)	—	sym. CH_3 stretch
—	—	2846(w)	CH_2 stretch
—	~1490(sb)	~1480(sb)	i.p OH deformation
1460(w)	—	—	asym. CH_3 deformation
1381(w)	—	—	sym. CH_3 deformation
1373(w)	—	—	—do—
—	~1360(sb)	~1350(sb)	i.p OH deformation
1150(w)	1150(w)	—	CH_3 rock
1050(s)	—	1055(s)	C-O stretch of tert. alcoholic group
912(w)	910(w)	—	C-O stretch of pri. alcoholic group
854(m)	860(w)	—	CH_3 rock
—	~650(wb)	~650(wb)	skeletal vibration
560(w)	570(w)	582(w)	o.o.p. OH deformation
—	375(m)	384(w)	Sm-O stretch
300(w)	—	320(w)	Sm-O stretch

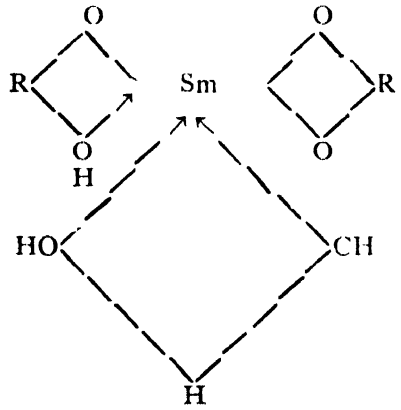
The structural formulae of the samarium glycolates under study may be written as



(SMG)



(SDG)



(STG)

where R = glycol residue and Pr^i = isopropyl group.

The various modes of vibrations of the various groups in the complexes have been discussed below :

OH stretching vibrations

In the present study of glycol derivatives of samarium, a broad band appearing at ~ 3400 cm^{-1} in di- and tri-glycolates has been assigned to associated (Kuhn, 1952) OH stretching vibrations. The broad shape is usually attributed to the fact that the glycolates associate (Sankhla & Kapoor 1965) in to various polymeric forms in which the molecules involved in hydrogen bonding to different extent, so that the broad band observed is composite of number of sharper bands.

OH deformation vibrations

Usually two broad bands are observed (Nakanishi 1962) in alcohols between 1500-1300 cm^{-1} which may be assigned to the in-plane deformation of the bonded OH. Also, broad and diffuse bands in liquid states in the region 750-600 cm^{-1} arise (Bellamy 1966) from the out-plane bonded OH deformation. In di-, and tri-glycolate of samarium, broad bands occurring at ~ 1480,

~1360, and ~650 cm^{-1}, therefore, have been assigned to in-plane and out-of-plane OH deformation, respectively.

C-O stretching vibrations

The C-O stretching vibrations due to primary, secondary and tertiary alcoholic groups have been found to appear (Bellamy 1966) in the region 1075-1000, 1125-1090 and 1210-1100 cm^{-1} respectively. SMG and STG possessing $-CH_2-O-$ group, and SDG possessing $\diagdown\!\!\!\!\diagup\!\!\!\!\diagdown\!\!\!\!\diagup$C-O- group have been found to absorb at 1060 and 1127 cm^{-1} respectively and therefore, have been assigned to C-O stretching vibrations of the respective group.

CH_3 and CH_2 group vibrations

In organic materials the asymmetrical and symmetrical C-H stretching modes of CH_3 group give rise (Bellamy 1966) to two bands at 2962 and 2872 cm^{-1}, respectively. In samarium mono-, and di-glycolates, a weak band at 2943 and 2960 cm^{-1} respectively, thus has been assigned to asymmetrical CH_3 stretching, while a band at 2872 cm^{-1} in samarium di-glycolate has been assigned to symmetrical CH_3 stretching.

In aliphatic compounds the asymmetric CH_3 deformation absorbs near 1465 cm^{-1} and the symmetric vibration near 1375 cm^{-1} (McMurry & Thronton, 1952). When there are two methyls on one aliphatic carbon atom, two bands with nearly equal intensity appear near 1385 and 1370 cm^{-1} due to in-phase and out-of-phase interaction of the two symmetrical CH_3 deformations (McMurry & Thronton 1952). In SMG a weak band at 1460 cm^{-1} and two bands at 1381 and 1373 cm^{-1}, therefore, have been assigned to asymmetric and symmetric CH_3 deformation respectively

Due to the interaction with skeletal streatching modes mehyl rocking frequencies are most sensitive and variable in position. In aliphatic compounds, CH_3 rock absorbs (Jones 1957) weakly at 1150-1120 cm^{-1} and 920-890 cm^{-1}. Two weak bands appearing at 1150 and 910 cm^{-1} in samarium mono-, and di-glycolates, therefore, have been assigned to CH_3 rocking vibrations

Two characteristic bands due to the in-phase and out-of-phase vibrations of the hydrogen atom of CH_2 group have been observed (Bellamy 1966) at 2926 and 2853 cm^{-1} respectively. Such bands in STG have been observed at 2930 and 2846 cm^{-1} and have been assigned to CH_2 group vibrations.

Skeletal vibrations

It has been pointed out by Simpson and Sutherland (Simpson & Sutherland 1949) that for isopropyl compounds a skeletal vibration could be predicted

near 850 cm^{-1}. A band at 854 cm^{-1} in SMG and a band at 860 cm^{-1} in SDG, therefore, have been assigned to skeletal vibration.

Sm-O vibration

The absorption bands below 700 cm^{-1} are generally ascribed to metal-oxygen stretching modes. A theoretical study (Nakamoto *et al* 1961) of different types of mental complexes (table 2) reveals that the number of infrared active vibrations are different for different types of metal complexes. The total number of such bands can give the geometry of the complex. In SMG, STG and SDG, two, three and two bands respectively have been observed in the region 600-250 cm^{-1}, indicating C_{2v}, D_3 and V_h symmetries for the respective glycolates.

Table 2. Symmetry of metal complexes and the number of ir-active (M-O) stretching vibrations

Types of metal complexes	Symmetry	Distribution of stretching vibs	No. of ir active vibs.
1:1	C_{2v}	$a_1 + b_2$	2
1:2 (square planar)	D_{2h}	$a_g + b_{1g} + b_{2u} + b_{3u}$	2
1:2 (tetrahedral)	C_{2v}	$2a_1 + b_1 + b_2$	4
1:3 (octahedral)	D_3	$a_1 + a_2 + 2e$	3

A close study of Table I reveals that the spectra of the glycol dervatives of samarium are almost idnependent of the co-ordination number of the metal in the region 4000-700 cm^{-1}, whereas in the region below 700 cm^{-1} they depend on it. A slight shift in the metal-oxygen stretching vibations towards the higher wave numbers with the increase in co-ordination number from three to four and six, indicates the small interaction between the ligand and the metal-oxygen vibrations.

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